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(54) TEXTILE FINISHING

(71) We, FARBWERKE HOECHST AKTIENGESELLSCHAFT, vormals Meister Lucius & Brüning, a Body Corporate recognised under German Law, of 6230 Frankfurt (M)-Hoechst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

The washing of textile materials with commercial detergents based on anionic surface active agents, for example alkylarylsulphonate, and non-ionic surface-active compounds, mostly blended with the usual builders, often results in the fact that the washed goods become hard and stiff. This behaviour of most of the detergents imparts the wearing properties of the goods and reduces their value as to usability.

It has been proposed in German Patent 902,610 to overcome these disadvantages by an after-treatment of the textiles with certain anionic and non-ionic surface active agents. German Patent 914,490 proposes, for the same purpose, an after-treatment of textile materials with higher molecular cationic compounds. However, the cationic products mentioned in this Patent either cause yellowing of the goods when applied repeatedly or they produce the required softening effect only when applied in large quantities. Quaternary ammonium salts with at least one long aralkyl or alkyl chain, which may be used as textile softening agents, are disclosed in the British Patent 1,098,793.

Belgian Patent 643,539 describes textile softening agents which contain, as the active substance, quaternary ammonium compounds with two long alkyl chains. The most important representative of this class of compounds is distearyl-dimethylammonium chloride which is now in widespread use. The softening effect of these dialkyl-dimethylammonium chlorides of the general formula

$$\left[\begin{matrix} C_nH_{2n+1} \\ C_nH_{2n+1} \end{matrix} \!\!>\!\! N\text{-}(CH_3)_2 \right]^+ Cl^-$$

becomes significant only when the alkyl groups have a chain length of from $n = 16$ upwards. The total number of carbon atoms of the long alkyl chains thus amounts to at least 32. The softening effect of these agents is excellent, but at the concentrations prescribed for use, the absorptiveness of the goods treated is strongly reduced. This disadvantageous effect can be observed in practice to an increasing extent, as housewives tend to overdose detergents. For terry towellings and underwear which is worn directly on the skin, such a reduction of the absorptiveness considerably impairs the usability and the wearing properties.

Many attempts were made to improve the capacity of cationic textile treating agents or of so-called soft rinsing agents to impart absorptiveness. The addition of non-ionic and even of cationic wetting agents, which was self-suggesting, did not bring the results hoped for. It was possible to obtain combinations with the mentioned additives that had improved absorptiveness-imparting properties, but these reduced

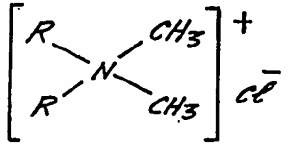
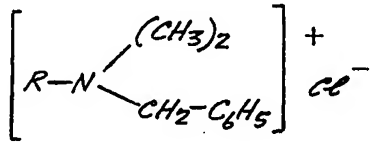
[*Price 25p*]

the softening effect. Neither could anionic auxiliary agents be used for improving the absorbing properties since they are liable to form insoluble electro-neutral salts with the cationic softener. It appeared as if softening effect and absorptiveness-imparting property would exclude each other.

Such compounds also have the disadvantage that they are sparingly soluble in water and must therefore be used in practical application together with certain dispersing agents and solubilising agents with the result that the softening action is occasionally reduced.

It has now been found in accordance with the present invention that cationic ammonium compounds with only one saturated or ethylenically unsaturated aliphatic chain with at least 18 carbon atoms in the cation, in which compounds the saturated or ethylenically unsaturated aliphatic chain with at least 18 carbon atoms is interrupted by at least one ether bridge, are excellent softeners whilst giving good absorbency and prove superior to the known products in respect of their water-solubility as can be seen from the Table which follows. Their use in practice can therefore take place without the addition of non-ionic dispersing agents which frequently impairs softening.

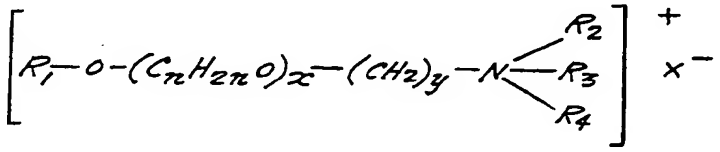
TABLE 1

Formula	R	Solubility in water 10%	1%	0.1%
	$C_{18}H_{37}$	paste	cloudy	cloudy
	$C_{20}H_{14}$	paste	precipitation	precipitation
$\left[R{-}O{-}(CH_2)_3{-}N{-}(CH_3)_3\right]^{+}Cl^{-}$	$C_{18}H_{37}$	pourable liquid	clear	clear
$\left[R{-}O{-}(CH_2)_3{-}N{-}\right)CH_3)_3\right]^{+}SO_4CH_3{-}$	$C_{20}H_{41}$	viscous liquid	clear	clear
$\left[R{-}O{-}(C_2H_4{-}O){-}(CH_2)_4{-}N{-}(CH_3)_3\right]CH_3COO^{-}{-}$	$C_{19}H_{39}$	viscous liquid	clear	clear

The subject of the present invention is thus a process for increasing the use value of textile materials, especially their softening, whilst giving good absorbency by treatment of the textile material with an aqueous solution of at least one cationic ammonium compound with only one saturated or ethylenically unsaturated aliphatic radical with at least 18 carbon atoms in the cation, wherein the saturated or ethylenically unsaturated aliphatic radical with at least 18 carbon atoms in the cation contains at least one ether bridge.

As a result of the ether configuration which induces hydrophilic properties and of the cationic character, the new soft rinses at the same time prevent the dreaded static charging of synthetic fibres. For example, nylon shirts rinsed with the new agents completely lose the troublesome charge on wear.

Laundry after-treatment agents used in accordance with the present invention are primarily cationic ammonium compounds of the general formula



in which R_1 is an alkyl radical with at least 12, preferably at least 16 carbon atoms, n is an integer of from 2 to 4, x is 0 or an integer from 1 to 3, y is an integer from 2 to to four, R_2, R_3 and R_4 each denote hydrogen or an aliphatic radical with less than 8 carbon atoms which may contain one or more hydroxyl groups and/or ether groups, and X^- represents an inorganic or organic anion, for example, halogen, acetate, benzoate, glycollate, lactate, sulphamate, sulphate, arylsulphonate, methosulphate and ethosulphate, the radical $R_1—O—(C_nH_{2n}O)_x—(CH_2)_y—$ however having to contain a total of at least 18 carbon atoms.

Suitable representatives of the laundry after-treatment agents used in accordance with the invention are listed under Nos. 1 to 8 in Table 2. They are manufactured by known methods.

The starting amines with the requisite ether bridge, from which the cationic ammonium salts used can be easily prepared, can be obtained from high molecular alcohols by reaction with acrylonitrile and subsequent hydrogenation

$$R_1OH + CH_2=CH—CN \longrightarrow R_1—O—(CH_2)_2CN \xrightarrow{H} R_1—O—(CH_2)_3NH_2$$

or from ether-carboxylic acids via the nitrile stage with subsequent hydrogenation

$$R_1O—(CH_2)_zCOOH \xrightarrow{NH_3} —R_1—O—(CH_2)_zCN \xrightarrow{H} R_1—O—(CH_2)_zCH_2NH_2$$

when R_1 may be C_{12} to C_{30} and $z=1$ to 5, or by amination of sulphated fatty alcohol oxyalkylates

$$R_1—O—(C_nH_{2n}O)_{v-1}—C_nH_{2n}O—SO_3Na \longrightarrow R_1—O—(C_nH_{2n}O)_{v-1}—C_nH_{2n}NH_2$$

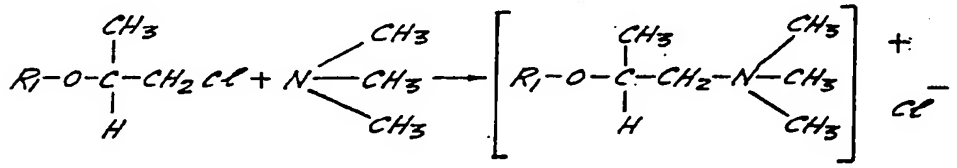
where $n=2$ to 4 and $v=1$ to 5.

When using dimethylamine, the corresponding tertiary amines are formed from the sulphated oxalkylates.

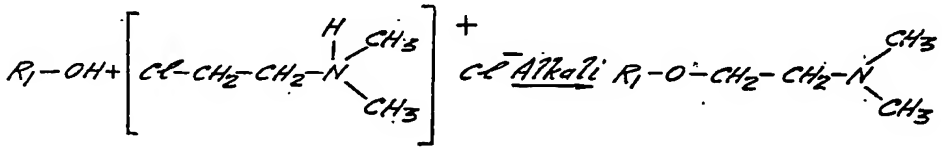
$$R_1—O—(C_nH_{2n}O)_{v-1}—C_nH_{2n}—N<\begin{matrix}CH_3\\CH_3\end{matrix}$$

The oxalkylsulphates used for amination may, for example, contain ethylene oxide or propylene oxide either by themselves or mixed with one another.

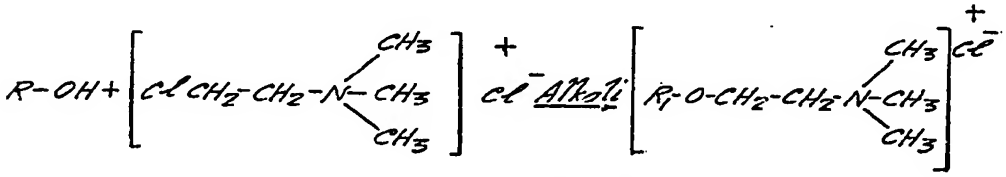
Instead of the sulphates, the corresponding chlorides of the oxalkylated alcohols may also be used for amination. When reacting such chlorides with, for example, trimethylamine, the quaternary alkyl-ether ammonium salts, particularly suitable for use as laundry after-treatment agents, are formed in one process stage.



Another way to synthesise the ether-amines used as starting substances is the condensation of fatty alcohols with tertiary β-chlorethylamines.



The resulting tertiary ether amines, after neutralisation with inorganic and organic acids, yield ether-ammonium salts suitable for use as soft rinses in accordance with the present invention. If condensation is carried out with quaternary β-chlorethyl ammonium salts, quaternary alkylether ammonium salts for use in accordance with the invention are obtained in one process stage.

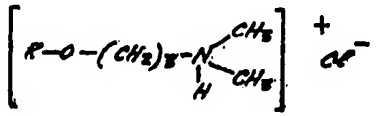
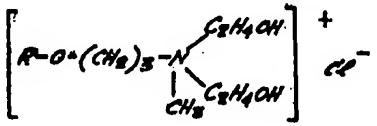
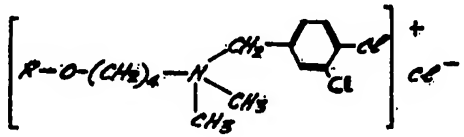


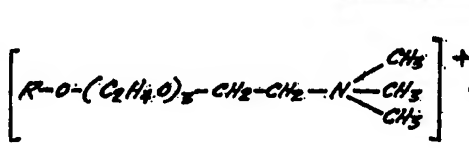
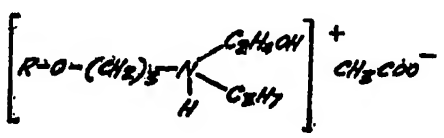
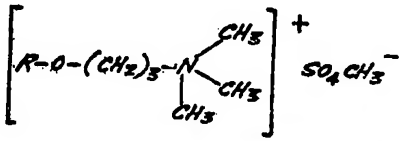
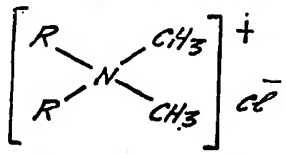
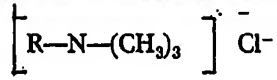
If the tertiary β-chlorethylamines are reacted with oxalkylated alcohols, then, after subsequent neutralisation or quaternisation with methyl chloride, ether-ammonium salts with at least two oxygen bridges are obtained which, because of the double ether function, exhibit good water solubility simultaneously with good softening and absorbency.

Higher molecular aliphatic alcohols with at least 16 carbon atoms especially serve as starting bases for the abovementioned ether-amines and the ether-ammonium salts in accordance with the invention. Suitable representatives are fatty alcohols and long chain synthesis alcohols from petro-chemistry which are available cheaply and in large amounts. The alkyl radical may be linear or branched. The OH group of the starting alcohols may be in the α-position or on any other carbon atom of the chain, or there may be used a mixture of alcohols in which the OH group position is randomly distributed.

The ether-ammonium compounds to be used in accordance with the invention may be added to the conventional rinses after the actual washing process. Appropriately, however, the products are used after the actual rinse. The amount added preferably lies between 0.1 to 1 g/l, especially between 0.1 to 0.3 g/l. The compounds may also be used for the final finishing of textiles, for example, by the padding process, in concentrations of from 2 to 50 g/l. The cationic ammonium compounds may also be applied to the textile materials in conjunction with other kinds of textile auxiliary agents, for example, optical brighteners or disinfectants.

Table 2 below shows the good action of the compounds in accordance with the invention (Examples 1 to 8) compared to a previously known product (Example 9) and the improved water solubility in comparison to a quaternary ammonium salt with only one long-chain alkyl radical, but without an ether bridge (Example 10).

Ex.	Cationic ammonium compound	R	Solubility	Handle	Smoothness with load	Smoothness without load	Absorptiveness 1′	Absorptiveness 5′	Absorptiveness 10′	Absorptiveness 20′
1	$\left[R—O—)CH_2)_3—N(CH_3)_3\right]^+ Cl^-$	$C_{18}H_{35}$	clear	very good	760	600	3	6.5	8	11
2		$C_{22}H_{43}$/ $C_{24}H_{49}$	clear	very good	760	550	2.5	4	5	8
3		$C_{18}H_{37}$/ $C_{20}H_{41}$	clear	very good	720	580	3	6	8	12
4		$C_{20}H_{41}$ $C_{22}H_{45}$	clear	very good	760	590	3.5	6.5	8.5	11
5	$\left[R—O—(C_2H_4O)—(CH_2)_3—N—(CH_3)_3\right]^+ Cl^-$	$C_{16}H_{33}$/ $C_{18}H_{37}$	clear	very good	780	600	3	6	8	12

Ex.	Cationic ammonium compound	R	Solubility	Handle	Smoothness		Absotrpiveness			
					with load	without load	1′	5′	′10	10′
6		$C_{20}H_{41}$	clear	good	860	630	4	7	9	11
7		$C_{24}H_{49}$/ $C_{26}H_{53}$	clear	very good	780	610	3	6	7	9
8		$C_{16}H_{33}$/ $C_{18}H_{37}$	clear	very good	800	600	3	6.5	8	10
9		$C_{16}H_{33}$/ $C_{18}H_{37}$ 30 : 70	cloudy viscous	very good	730	580	1	1.5	1.5	2
10		$C_{16}H_{33}$	cloudy	moderate	880	740	4	7	8	10

The values indicated in the Table for handle, smoothness and absorptiveness were determined as follows:

Handle:

The handle was evaluated subjectively on terry towelling washed in the usual manner and after-treated at a goods to liquor ratio of 1:10 at a concentration of 0.1 g/litre.

Smoothness:

The smoothness was determined on a selected nettle fabric according to the method described by H. Carlhoff in the journal "Wäschereitechnik und -chemie" 18, page 482 (1965). The smoothness was determined with load (w.l.) and without load (without l.).

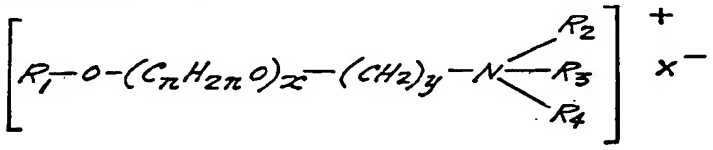
Absorptiveness:

The absorptiveness of the textile materials treated was determined according to the ascension-height method In this method, the height of the ascension of water in the textile material was determined under constant conditions as a function of time. The values indicated represent the ascension-heights in cm measured after the periods of time indicated, i.e. 1, 5, 10 and 20 minutes. The textile material used was cotton cambric. The textile material to liquor ratio was 1:10 with a concentration of softening agent of 0.2 g/litre.

WHAT WE CLAIM IS:—

1. A process for softening textile materials and improving the wearing properties of textile materials, wherein the textile material is treated with an aqueous solution of at least one cationic ammonium compound containing only one saturated or ethylenically unsaturated aliphatic radical with at least 18 carbon atoms in the cation, wherein the saturated or ethylenically unsaturated aliphatic radical with at least 18 carbon atoms contains at least one ether bridge.

2. A process as claimed in claim 1, wherein at least one cationic ammonium compound of the general formula



in which R_1 represents an alkyl radical which has at least 12 carbon atoms with the condition that the group $R_1—O—(C_nH_{2n}O)_x—(CH_2)_y—$ has a total of at least 18 carbon atoms, n represents an integer from 2 to 4, x represents 0 or an integer from 1 to 3, y represents an integer from 2 to 4, each of R_2, R_3 and R_4 represents hydrogen or an aliphatic group which may contain one or more hydroxy and/or ether groups and which contains less than 8 carbon atoms, and X^- represents an inorganic or organic anion, is used.

3. A process as claimed in claim 2, wherein at least one cationic ammonium compound of the formula given above is used, in which R_1 represents an alkyl radical which has at least 16 carbon atoms.

4. A process as claimed in claim 2 or 3, wherein X^- represents a halide, acetate, benzoate, glycollate, lactate, sulphamate, sulphate, arylsulphonate, methosulphate or ethosulphate anion.

5. A process as claimed in claim 1, wherein there is used a cationic ammonium compound as defined in any one of Examples 1 to 8 herein.

6. A process as claimed in any one of claims 1 to 5, wherein the concentration of the cationic ammonium compound or compounds is within the range of 0.1 gram per litre to 1 gram per litre.

7. A process as claimed in any one of claims 1 to 5, wherein the concentration of the cationic ammonium compound or compounds is within the range of 0.1 gram per litre at 0.3 gram per litre.

8. A process as claimed in any one of claims 1 to 7, wherein the cationic ammonium compound is used together with an optional brightener, a disinfectant or more than one such substance.

9. A textile material whenever treated by a process as claimed in any one of claims 1 to 8

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